

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

In re Application of
Thomas Ostrowski, et al
Serial Number 10/515,350
Filed: June 6, 2003
For: PREPARATION OF POLYETHER POLYOLS

DECLARATION UNDER 37 CFR 1.132

I, Thomas Ostrowski, a citizen of the Federal Republic of Germany and residing at Mannheim, Federal Republic of Germany, declare as follows:

I am a fully trained chemist, having studied chemistry at the University of Bochum, Germany, from October 1989 to January 1995,

I received my Doctors degree from the said university in 1998,

I joined BASF Schwarzheide GmbH of 01986 Schwarzheide, Federal Republic of Germany, in 1998, since when I have been working in the field of polyurethane research and development,

I am well acquainted with technical English,

I am one of the inventors of the patent application Serial Number 08/859,993 and therefore acquainted with the field to which the said application relates.

To demonstrate the difference between the continuous and discontinuous ethoxylation of a continuously produced DMC-catalyzed polyether polyol intermediate, I made the following experiments:

Experiment 1: Synthesis of KOH-catalyzed polyol

1,5 kg Glycerine were charged into a 20 L pressure resistant reactor equipped with a two stage cross blade agitator (rotating speed: 250 1/min). Subsequently, 0,0562 kg solid KOH were added. After the reactor had been purged with nitrogen, the reactor was heated up to 120 °C and water was removed at 7 - 9 mbara for 3 hours. The water content of the alcoholate was thereby reduced to about 0,1 %.

The reactor pressure was adjusted to 1 bara and 17,59 kg propylene oxide were charged via a dipped pipe into the reactor within 4 h. After the propylene oxide addition had been stopped, the reaction mixture was allowed to react for additional 4 h, until the reactor pressure was constant.

The reactor content was cooled down to 90 °C and 940 g Macrosorb MP-5 plus and 375 g water were added. After stirring for 2 h at 90 °C, the temperature was raised to 100 °C and the water was removed at 1 mbara. The solids were filtered off from the product using Seitz filters. The final product had a water content of 0,016 wt-%. The OH-number of the product was determined to be 112,6 mg KOH/g. The content of residual potassium was less than 2 ppm, the acid number of the product was 0,002 mg KOH/g. This product is designated as "VP1485-KOH".

Experiment 2: Synthesis of DMC-catalyzed polyether polyol precursor

A 300 L reactor equipped with cross blade agitators was charged with 25 kg of the KOH catalyzed polyol "VP1485-KOH" obtained in Experiment 1. 0,0625 kg DMC catalyst, prepared according to EP-B 0 862 947, in the form of wet filter cake was added. The reactor was heated under nitrogen atmosphere and water was removed from the suspension at 120 °C and 1 mbara. The water content was thereby reduced to 0,023 wt-%. Subsequently, the reactor temperature was raised to 130 °C and 13,88 kg Glycerine and 211,13 kg propylene oxide were added simultaneously via separated dipped pipes into the reactor at 120 °C. The ratio of both feed streams was kept constant. After the addition of the feed streams had been completed, the reaction mixture was allowed to react for 30 minutes until the reactor pressure remained constant. The OH-number of the product was determined to be 114,2 mg KOH/g. This product is designated as "VP1485-DMC".

Experiment 3: **Continuous propoxylation to give a polyether polyol intermediate**

The continuous propoxylation of the “VP1485-DMC” product obtained in Experiment 2 was performed in a CSTR reactor having a volume of 1,25 L equipped with a two stage agitator (bottom: disc agitator, top: cross blade stirrer, rotation speed: 700 1/min). In order to control the degree of filling, two thermocouples were immersed into the reactor at two different heights (difference: 1 cm). The reactor outlet was connected with a gear pump, the rotation speed of which was controlled by the temperature of the two thermocouples. In order to measure the content of non-reacted propylene oxide, a ATR-IR probe (Mettler-Toledo ReactIR, diamond probe) was immersed into the liquid phase of the reactor.

Initially, 500 mL “VP1485-DMC” obtained in Experiment 2 were charged into the reactor and heated up to 130 °C. Addition of “VP1485-DMC” was started (0,3 kg/h), the bottom valve still closed. After the filling level had reached 1 L, the bottom valve was opened and the gear pump started. Addition of propylene oxide (0,699 kg/h) was started. The residence time in the reactor was about 1 h. The product mixture was fed into a vessel which was operated under reduced pressure (10 mbara, 130 °C) in order to remove non-reacted propylene oxide. After 12 h operation time (12 residence times), the degassed product was fed into a second stripping vessel and stripped for additional 1 h. The product had an OH-number of 34,2 mg KOH/g. It is designated as “VP4950-DMC”.

Experiment 4: **Continuous ethoxylation of the polyether polyol intermediate**

In order to perform the continuous ethoxylation, 20 kg “VP4950-DMC” obtained in Experiment 3 were charged into a 25 L vessel. 0,092 kg KOH (as 48 wt-% aqueous solution) were charged and water was removed at 120 °C and 10 mbara for about 3 h. The catalyst containing product was stored in this vessel.

The ethoxylation reactor was a 25 m stainless-steel tube having an inner diameter of 3 mm and having the shape of a coil. This reactor coil was placed into a 50 L barrel containing water at 80 °C. The reactor coil was equipped with two injection points for EO, one of them positioned 10 cm downstream of the reactor inlet and the other one 5 m downstream of the reactor inlet. EO was charged using two HPLC pumps. The pressure in the reactor was kept at about 20 bara by means of a pressure keeping valve. Downstream to the pressure keeping valve, a vessel was placed which was operated at 10 mbara and 120 °C in order to collect the product and to remove remaining ethylene oxide.

The catalyst containing product from the storage vessel was fed into the reactor by means of a gear pump. The flow of the feed was adjusted to 1 kg/h. Ethylene oxide was added via the injection points. The flow rate was 50 g/h at each injection point.

The ethoxylated product was collected. The catalyst was removed following the procedure of Experiment 1. The product had an OH-number of 31,1 mg KOH/g, the ratio M_w/M_n was 1,3 and the content of primary OH-groups, determined via NMR after reaction of the polyol with 2,2,2-trichloroacetylisocyanate (CAS 3019-71-4), was 69 mol-%. The product was clear, the turbidity index was determined using a Hach Ratio/XR nephelometer to be 3,0 NTU units (nephelometric turbidity units according to ISO 7027).

Experiment 5 (for comparison): **Discontinuous (semi-batch) ethoxylation of polyol intermediate**

For comparison, the product of the continuous propoxylation "VP4950-DMC" obtained in Experiment 3 was ethoxylated in the semi-batch mode. 13,5 kg "VP4950-DMC" were charged into a 25 L reactor and 0,092 kg KOH (as 48 wt-% aqueous solution) were added. Water was stripped off at 120 °C and 10 mbara for 3 h. Subsequently, 3,5 bar nitrogen was added in order to provide an inert atmosphere. 1,5 kg ethylene oxide were added within 1 h. The reaction mixture was allowed to further react for 30 min. The product was neutralized following the procedure of Experiment 1 using Macrosorb and water. The final product had an OH-number of 30,95 mg KOH/g. The primary OH-content was 71 %, determined via NMR after reaction of the polyol with 2,2,2-trichloroacetylisocyanate. The product was cloudy, the turbidity index was determined using the Hach Ratio/XR nephelometer to be 29 NTU units.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed at 67056 Ludwigshafen, Germany, this 9th day of August 2006



Signature of Declarant